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Various Pesticide Residues Especially Organochlorine and Organophosphorous Pesticides in Water of River Jhelum at Srinagar City in Kashmir Valley (India)

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ABSTRACT

The River Jhelum is a famous river located in the northern region of India i.e. in Kashmir valley. It is a tributary of the Chenab River which flows in India and Pakistan with a total length of 505miles (813km). The river Jhelum has been subjected over the years to tremendous pressure due to discharge of untreated sewage, industrial effluents, residues of pesticides and impartment insecticides which may result in affect of ecological health of the river. The objective of this study was to identify and quantify of some pesticides both organochlorine and organophosphorous present in water of river Jhelum in Kashmir valley. These pesticides are mainly used to control the soil and crop pests in agricultural fields and direct damping of wastes into river systems. These pesticides have some physical and chemical properties such as, low aqueous solubility; water partition coefficient and persistence in the environment make them capable of long range transport. In this study collection of water samples are taken from three sites (upstream, mid stream and down- stream and finally analyzed for their pesticide profile. Various extractions like, liquid-liquid extractions, GE-ECD where used for the determination of these compounds. Pesticides likes of endosulfan, methyl parathion and DDT where observed in higher concentration of water samples collected from river Jhelum in Kashmir valley of India. Especially the concentration of DDT was quiet high which might be due to slow degradation of DDT in soil i.e. 80-100% in 4-35 years.

Keywords: Jhelum, Kashmir, Organophosphorous, Organochlorine, Water, Sediment etc.

INTRODUCTION

The substances intended for preventing, destroying, repelling any 'pest' are known as pesticides. Pesticides are special kinds of products for crop protection. Generally, pesticides are chemical or biological agents (such as virus, bacterium, antimicrobial or disinfectant). Many pesticides of different chemical nature are currently used for agricultural purposes all over the world. Due t this wide spread use they are detected in various environmental matrices, such as water, soil and air. Pesticides are divided into number of classes, of which the important are Organochlorine and organophosphorous compounds. Among the two main classes, organochlorine pesticides resist biodegradation and they can be concentrated through food chains and produce a significant magnification of the original concentration and the end of the chain. Due to this residence time of these substances in the environment, there is a great interest in examining the pollution they cause. On the other hand, organophosphorous pesticides are known to degrade rapidly depending on their formulation method of application, climate and the growing stage of the plant.

The general progression of pesticide development has moved from highly toxic, persistent and bio-accumulating pesticide such DDT, to pesticide that degrade rapidly in the environment and are less toxic to non-target organisms. The developed countries have banned many of the older pesticides due to potential toxic effect to man or their impact on ecosystems, in favor of more pesticide formulations. Organochlorine pesticides are cheapest to produce in developing countries and remain highly effective for some purposes. Developing countries maintain that they cannot afford, for reason of cost or efficacy, versus ecological impacts, including long range transport, and access to modern pesticides formulations at lost cost remains a contentious global issue. In Kashmir valley of India there are numerous apple gardens and the farmers uses many pesticides such as DDT to kill pests. Pesticide residues reach the aquatic environment through direct runoff, leaching and careless disposal of empty container, equipment washing etc[1]. Pesticides like DDT and HCH were used extensively in India till recently both for agricultural and sanitary purposes. It is estimated that about 25000 MT of chlorinated pesticides were used annually in India and DDT accounted for 40% of this group[2]. In India, the concentration of these pesticides have been detected in almost all segments of environment due to their extensive use in past, which have shown potential to biomagnified/ accumulate in animal tissue, human blood, adipose tissue and breast milk [3].since the pesticides are lipid soluble in nature, cumulative accumulation of low of these in the body fat of mammals might pose potential hazards in long run[4]. Srinagar city of country India lies on the geographical coordinates of 22° 57' 0" N, 79° 31' 0" E. Srinagar is located in center of the Kashmir Valley set on the banks of River Jhelum. Covering a total area of 294 square kilometers, it is located at an altitude of 1585 meters above sea level. It is surrounded by Kargil and Ganderbal in the north, Pulwama in the south, and Budgam in the north-west. Srinagar city receive about 3 mega gallons of untreated waste water per

day including effluents from urban settlement, dying industry, silk industry(Raj Bagh), hospital (LD Hospital) and pathological laboratories etc. besides most of the residents in the neighboring districts of Srinagar city are farmers and their livelihood depends on their agricultural produce. The main of research was to carry out systematic study on identification and quantification of some pesticide residues in both water and sediment of River Jhelum. The results obtained from this study are presented in this paper.

MATERIAL AND METHODS

Analytical procedure

Liquid-liquid extraction followed by gas chromatographic detector 5 and 10 with some modification was used for the determination of pesticides residues. 1 liter of water sample was filtered using 0.45-µm whatman glass fiber filter paper (washed in acetone and dried in oven overnight). To this 50ml of phosphate buffer was added and pH was maintained to 7. Now mixture of diethyl ether and hexane in sulphate and made up to 5 ml with hexane.

The samples thus prepared were injected and analyzed. The pesticides standards (99.9%) purity was supplied from Aldrich Chemicals Germany. Using standard samples containing known amounts of pesticides, accuracy of the determinations was routinely checked. All analysis were carried out in duplicate and recoveries of individual pesticides were determined through spiked sample method, which were found between 98-99.5%. Recovery correction factors were applied to the final results. The results obtained for the various water samples are presented in Tables 3 and Fig. 4.

Study area

A total of three sampling locations were selected on the river Jhelum depending upon presumed water quality and extent of pollution. They were Zero Bridge Rajbagh (site I, upstream), Budshah Chowk Lalchowk (site II, midstream) and cement Kadal Noor-Bagh(Site III, downstream). The satellite of three sites of river Jhelum is shown in Fig 1.

Sample Collection

The water sample of the river was collected in sterilized plastic container. Duplicate samples for pesticide measurement were collected from each sampling location. The containers were carefully filled just to overflowing, without passing air bubbles through sample or trapping air bubbles in sealed container. Preparation of the containers included washing with detergent rinsing with tap water and air drying. The collected samples were preserved in an icebox and transported to laboratory for analysis. After transportation to laboratory, samples were stored at -18°C and extraction was done within 50 hours. Sampling was carried for one and half years on seasonal basis for the period of January 2011 to June 2012. Samples were analyzed in the chemical laboratory of IIIM Jammu and Department of Chemistry A.P.S.U Rewa, M.P.

Chemicals and Instrumentation

The solvents used for extraction i.e. diethyl ether and hexane were obtained from Aldrich Chemicals Germany. The pesticide

residues were analyzed by gas chromatography (GC) supported by electron capture detector (ECD). The laboratory used Varian GLC. Nitrogen gas used as the carrier gas and makeup gas and the injection technique was in the split mode. The GC conditions used are furnished in Table 1. The retention times obtained for the various pesticides residues are given in Table 2 and Fig.2. The ratio of 1:1 was taken in a 2 liter separating funnel, and 1 liter of water sample mixed with phosphate buffer was added to it and was shacked vigorously. The layers were allowed to settle down and pass through separating funnel and collected. The extraction was repeated thrice and the solution obtained was filtered with a little amount of sodium sulfate. The combined extracts were filtered and concentrated in a vacuorotary evaporator.

RESULTS AND DISCUSSION

It is well known that most of the applied pesticides are subject to many transport and conversion products. Thus they do not remain at their target site but often enter aquatic environment via soil percolation, air drift or surface runoff affecting abundance and diversity of non-target species producing complex effect on the ecosystems and altering tropics interactions[5].

The results of the analysis of the water samples from river Jhelum at Srinagar city have shown the presence of both organochlorine and organophosphate pesticides. The compounds detected were Methyl-parathion, Endosulfan, DDT, and Lindane.

Concentration of organochlorine and organophosphate pesticides (Endosulfan, Lindane and DDT and its metabolites) in water of Jhelum river, during different season of study period (Jan.2011-June 2012) are summarized in Table 3 and Fig. 3.

It has been reported that though DDT is banned but it is a part of many organochlorine insecticides, which are not banned. DDT shows slow degradation therefore its concentration remains high in the environment[6].

Lindane is an organochlorine also known as BHC and HCH. The solubility of lindane in water is $10mgl^{-1}$ and reported half-life of 18 hours. The concentration of lindane in river water is low as compared to other pesticides studied. The concentration of lindane in river water ranged from ND to 74, $04ng^{-1}$.The order of the concentration of lindane at different sites in river was: site II > site I= site III. Methyl parathion is an organophosphate and is used extensively in agriculture and pest control programs. Methyl parathion being an organophosphate is very toxic for mammals as well as aquatic organisms. In mammals it damages nervous system and in fishes it causes deformation but in the entire seasons Methyl- parathion was absent in the water of river Jhelum. Endosulfan is an organochlorine and highly toxic pesticide in EPA toxicity. The solubility of endosulfan is $0.3mg^{-1}$ with a half life of 5 weeks in water but its isomer i.e. β isomer has longer half-life i.e. 150days under neutral conditions. Though endosulfan is banned in many countries but it is extensively used in India. In the present study, T. Endosulfan ranged from BDL to 739 ngl^{-1} in river sediments. High concentration of endosulfan was present in the water of river. A- Endosulfan was higher in water samples, the concentration varying

from BDL to 739 ngl^{-1} whereas β-Endosulfan was in the range of ND to 157.30 ngl^{-1} in river water. The high concentration of α Endosulfan in water than β Endosulfan in river might be explained as α and β Endosulfan are conformational isomers and cane be interconnected without breaking bonds. T-Endosulfan was maximum at site II. This might be due extensive use of these pesticides in agricultural activities by farmers and being an organochlorine it has also tendency to accumulate in the river sediments. Endo-sulfan is one of the most toxic pesticides, responsible for many fatal pesticides poisoning. Endosulfan is a xenoestrogen an endocrine disruptor, causing reproductive and developmental damage in animals and humans. It is a neurotoxic in insects and mammals. Endosulfan is highly toxic for aquatic organisms and has bioaccumulating effect especially in fish. The concentration of T- Endosulfan in river water was: site II > site I > site III.

The discharge of agro-chemicals from flood plains, due to raining, agriculture fields through agricultural runoff might have contributed to the elevated pesticide concentration at site II. The increased concentration of DDT at site II in water of river might be due to discharge of medical wastes from Lal Ded Hospital, which is channelized directly into river near old J and K board office Lal Mandi. Hospitals use DDT for public health activities, incidents. DDT is an organochlorine insecticide nearly insoluble in water with a half-life 2-15 years and is immobile in most soils. It is a persistent organic pollutant. DDT along with its isomer o, p' and p, p'- DDT were present and o, p'- DDT in water of river Jhelum. This might be attributed to easy metabolization of DDT to its metabolites, which are more stable and persistent than parent molecules of DDT. DDT was present at all the sites in river water. The present result indicates that there is predominant use of DDT in the study area, which as agricultural runoff or surface runoff contributes to a heavy load of pesticide pollution in water.

DDT and its metabolic products magnify through the food chain and stored mainly in the body fat. DDT is classified as "moderately toxic" by US National Toxicological Program and "moderately hazardous" by WHO. DDT is highly to aquatic life especially fishes as it can be bioaccumulate leading to long-term exposure to high concentrations. In human beings, the higher concentration of DDT leads to neurophysiological and psychiatric symptoms. The order of concentration of T-DDT obtained in river water was: site II > site III > site I.

So it is clear from the above discussion that the order of the concentration of these pesticides in water of river Jhelum varied from site to site, and from one location to another location. The presence of DDT metabolites and BHC in the river indicates continuous use of DDT in the catchments. It is noted that though these pesticides are banned in other countries but DDT and BHC are in restricted use in India[7].

Thus we can say that a using pesticide effectively while maintaining water quality presents an important challenge and is need of the hour. As citizens, we must recognize the significant role of pesticides in maintaining a high quality of life.

Table- 1: Column specification and operating condition of gas Chromatograph

Detector	**Electron Capture Detector (ECD)**
Column specification	30m×0.25m×0.25µ Cpsil-5-CB
Injection port temperature	279° C
Detector temperature	300° C
Column Programming	169° C hold for 2 min@ 3° C/ min 210V hold for o min @ 30° C min 270° C hold for 2 min Total retention time 20.33 min
Carrier gas	N_2 flow
Split ratio	9:1
Carrier gas flow rate	2 ml/min
Back up flow	27 ml/min
Injection volume	2µl
	Total volume of sample Water- 2 ml. Soil- 5ml

Table 2: Retention Time for the pesticides analyzed by the Gas Chromatograph

S. No.	Pesticides	Retention Time (R.T.) (In min.)
1	Lindane	3.50
2	Methyl-Parathion	4.67
3	α- Endosulfan	8.70
4	β- Endosulfan	10.57
5	o, p' – DDT	11.70
6	p, p'- DDT	13.18

Table 3: Seasonal Pesticides concentration in Jehleum river water Zero bridge Raj Bagh (Site I). Budshah chowk(Site II) and Cement Kadal Noor bagh (Site III) Jan. 2011- June 2012.

Sites	Seasons	Lindane	Metyl Parathion	α- Endosulfan	β- Endosulfan	T- Endosulfan	o, p' – DDT	p, p'- DDT	T-DDT
Site 1	Summer	BDL	ND	168.03	ND	168.03	ND	ND	ND
Site 1	Monsoon	BDL	ND	BDL	BDL	BDL	78.20	ND	78.20
Site 1	Winter	BDL	ND	108.04	108.04	108.02	56.71	ND	56.71
Site 1	Summer	BDL	ND	131	ND	131	ND	ND	ND
Site 1	Monsoon	ND	ND	BDL	BDL	BDL	488	ND	488
Site 1	Winter	ND	ND	140	BDL	140	488	ND	488
Site II	Summer	BDL	ND	BDL	125.07	ND	ND	ND	ND
Site II	Monsoon	74.02	ND	512.10	BDL	BDL	ND	ND	ND
Site II	Winter	BDL	ND	207.03	ND	207.03	ND	ND	ND
Site II	Summer	ND	ND	BDL	156.29	156.29	ND	ND	ND
Site II	Monsoon	48.28	ND	7.38	ND	738	ND	ND	ND
Site II	Winter	BDL	ND	738	ND	738	ND	ND	ND
Site III	BDL	BDL	ND	144	BDL	145	ND	ND	145
Site III	Monsoon	ND	ND	BDL	BDL	BDL	112	ND	212
Site III	Winter	ND	ND	129.08	BDL	129.08	BDL	ND	124
Site III	Summer	BDL	ND	BDL	BDL	BDL	ND	ND	ND
Site III	Monsoon	BDL	ND	BDL	BDL	BDL	BDL	ND	ND
Site III	Winter	BDL	ND	BDL	BDL	BDL	BDL	ND	ND

BDL= Below detection limit, ND= Not detected, Detectable limit: Lindane = 1.0. Me. Parathion= 10.00, α- Endosulfan and β- Endosulfan= 10.00, o, p' – DDT and p, p'- DDT= 1.00. All values in nanogram/liter.
(Analysis done at Chemical laboratory of IIIM Jammu using Varian GLC).

Figure 1: Satellite imagery of River Jhelum in Srinagar city

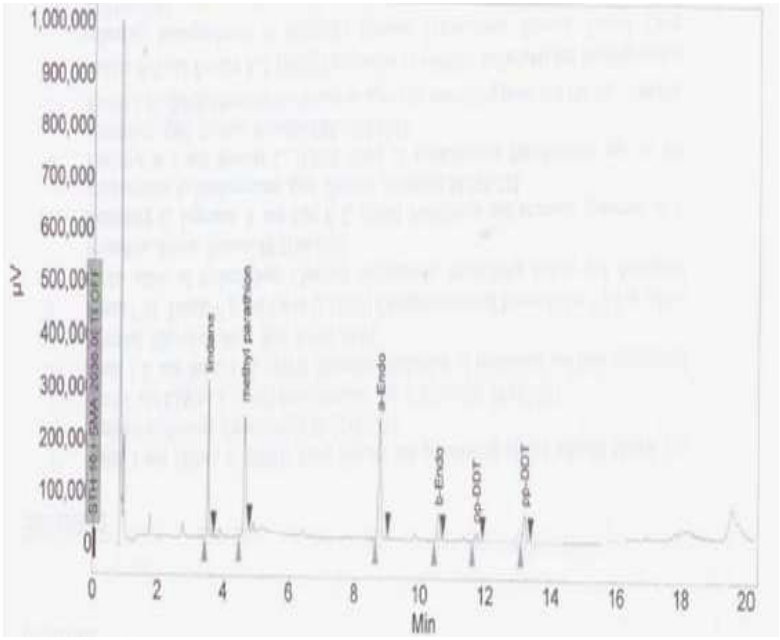

Fig. 2 Chromatogram showing retention time for six different Pesticides (Organochlorine and Organophosphate)

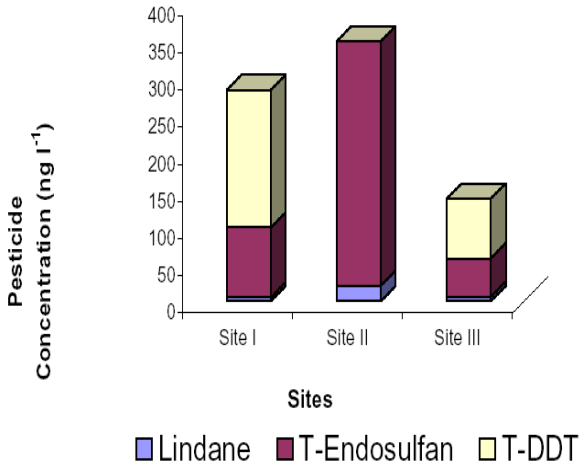

Figure 3: Range of Concentration of Pesticide in water of River Jhelum (Jan.2011- Jun. 2012)

CONCLUSION

So from the above study we can conclude that the River Jhelum gets polluted day by day due to discharge of toxic heavy metals and pesticides from the point and non point sources. As these toxic substances don not degrade, they remain persistent in the environment, and also have the ability to bioaccumulate in the food chain, which might pose potential hazards in long run.

The present study was first known analysis of Organochlorine (OCPs) and Organophosphates (OPPs) pesticide distribution in water of river Jhelum. The water of river Jhelum is polluted by these OCPs and OPPs. A relatively high level of these compounds was observed in most study areas. Most of the organochlorine pesticides found in this study were officially banned but they were still seen in the river. Regular monitoring and strict law enforcement is needed to develop a strategy to manage the environmental hazards due to these elements and improve environmental protection of this area. Further it is also suggested that we only take four pesticides into consideration in this present study but there exists number of pesticides in the river of Jhelum which were not taken into consideration and were not analyzed in this study, so further work is needed to determine the bioaccumulation of these toxic elements in the food web and the associated risks to the ecosystem and human health.

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